Suitable Biomass for a Sustainable Sugarcane Industry

The lignocellulosic fraction of Sweet Sorghum

Introduction

As discussed in Update 5 the extractives from sweet sorghum can be used for various applications. The extractives from sweet sorghum is dominated by soluble sugars but more than 130 metabolites can be routinely identified in the fraction. Hover, this fraction represents less than 40% of the total biomass.

To consider the full biomass potential of sorghum we need to analyse and evaluate it as a feedstock for first and second generation biofuels, extraction of water soluble components, or for biogas applications. This particular project was initiated to consider Sorghum as a supplementary biomass source to address the bagasse shortfall at the Mossman Mill.

Here we consider the possibilities of using sorghum as a feedstock for second generation biofuels and anaerobic digestion.

In this Update

- *The sweet sorghum lignocellulosic feedstock*
- *Biofuel after enzymatic hydrolysis of lignocellulose*
- *Biofuel after gasification*
- *Anaerobic digestion*

Biomass composition

The lignocellulosic fraction of the five sweet sorghum genotypes tested in this study makes up 62% of the total biomass (Fig. 1). The composition, and potential uses of the water soluble fraction, were previously discussed.
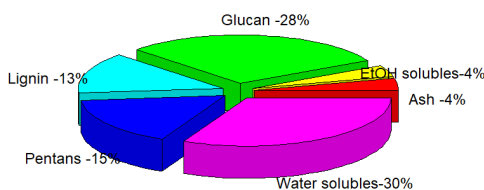

Figure 1: *Pie chart of the average biomass composition of sweet sorghum grown for 70 DAP under tropical conditions. Values represent the composition of the entire above-ground biomass*

The lignocellulosic fraction is made up of glucan (46%), pentans(25%), lignin (20%) and ash (6%) (Fig. 2). Ash is the residue that remains after the material

has been incinerated. The main component in the pentan fraction is xylose.
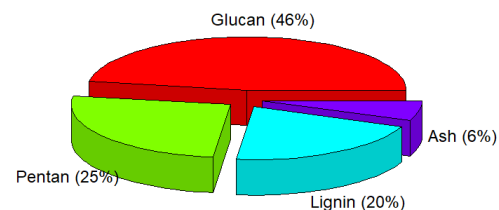

Figure 2: *Pie chart of the average lignocellulosic composition of sweet sorghum grown for 70 DAP under tropical conditions. Values represent the composition of the entire above-ground biomass*

Ash has no energy value but can cause problems in many thermochemical processes (e.g. pyrolysis, gasification, and combustion). The lignin fraction that we report here is the combination of acid soluble and acid insoluble (Klason) lignin. These values are similar to previous reports on sweet sorghum [4, 1]. The average ratio be-

tween Klason and acid soluble lignin is 7.5:1.

Biofuel conversion processes

Producing advanced biofuels typically involves a multi-step process. Firstly, the tough rigid structure of the plant cell wall which includes the biological molecules cellulose, hemicellulose, and lignin must be broken down. This can be accomplished in one of two ways: high temperature deconstruction or low temperature deconstruction.

High-temperature Deconstruction

Deconstruction is accomplished by using extreme heat and pressure to break down solid biomass into liquid or gaseous intermediates. Here we only consider two primary routes that can be used in this pathway:

- Pyrolysis
- Gasification

During pyrolysis, biomass is heated rapidly at high temperatures (500^oC–700^oC) in an oxygen-free environment. The heat breaks down biomass into pyrolysis vapor, gas, and char. Once the char is removed, the vapors are cooled and condensed into "bio-crude" oil.

Gasification follows a slightly similar process; however, biomass is exposed to a higher temperature range ($>700^oC$) with some oxygen present to produce synthesis gas (or syngas)—a mixture that consists mostly of carbon monoxide and hydrogen.

Low-Temperature Deconstruction

Deconstruction typically makes use of biological catalysts called enzymes or chemicals to breakdown feedstocks into intermediates. First, biomass undergoes a pretreatment step that makes sugar polymers like cellulose and hemicellulose more accessible. These polymers are then broken down enzymatically or chemically into simple sugar building blocks during a process known as hydrolysis.

Upgrading

Following deconstruction, intermediates such as crude bio-oils, syngas, sugars, and other chemical building blocks must be upgraded to produce a finished product. This step can involve either biological or chemical processing.

Microorganisms, such as bacteria, yeast, and cyanobacteria, can ferment sugar or gaseous intermediates into fuel blend stocks and chemicals. Alternatively, sugars and other intermediate streams, such as bio-oil and syngas, may be processed using a catalyst to remove any unwanted or reactive compounds in order to improve storage and handling properties.

Biofuel after enzymatic hydrolysis

There are several potential routes for hydrolysis of biomass before conversion of the sugars to ethanol.

Here we only consider two options. The first is based on dilute acid hydrolysis of biomass in two plug-flow re-

actors. This can be considered to representative of a near-commercial dilute-acid hydrolysis facility.

The second is enzymatic hydrolysis of biomass. This involves a dilute acid pre-treatment and separate fermentation of the monosaccharides from cellulose and hemicellulose (sequential hydrolysis and fermentation-SHF). Cellulase enzymes are produced in a separate reactor to that for hydrolysis. This is the likely setup of the first commercial enzymatic hydrolysis facilities.

Ethanol yield from cellulose was calculated by using Eq:1 and from hemicellulose by using Eq:2 (see Table 1).

$$E_{cl} = \left(\frac{1110^a * 0.511^b}{0.789^c}\right)\left(\frac{100 - Cl_{con}}{100}\right)\left(\frac{H_{cl}}{100}\right)\left(\frac{F_{gl}}{100}\right) \quad (1)$$

$$E_{hc} = \left(\frac{1136^d * 0.511^b}{0.789^c}\right)\left(\frac{H_{hc}}{100}\right)\left(\frac{F_{hc}}{100}\right) \quad (2)$$

The data shows the superiority of technology (Tech2), that sequentially hydrolyse and ferment the released sugars (Fig. 3).
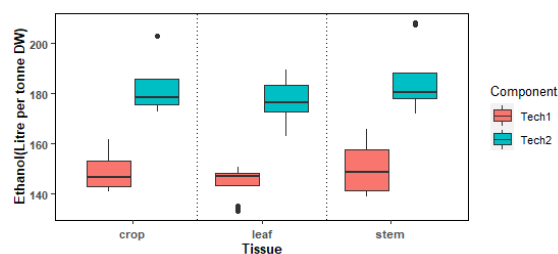

Figure 3: *Potential ethanol yield from sorghum using two fermentation technologies.*

Because the lignocellulosic fraction of the leaves and stems do not differ significantly (P>0.05) there is no advantage in separating leaf and system material for this type of application. Previous work has also shown that leaf removal is not feasible on an industrial scale and utilising the whole crop does not influence ethanol yields [3].

Biofuel based on gasification

Unlike the hydrolysis technologies, which specifically target the structural polysaccharides, the thermochemical processes degrade all volatile components including lignin. Determinations of process yields for these technologies are based on the estimated heating values of the feedstock.

The Higher Heating Value (HHV) is calculated from the ash, carbon, and hydrogen content

$$HHV(MJKg^{-1}) = 1.3675 + 0.3137C + 0.7009H + 0.318O^* \quad (3)$$

Where O^* = the sum of the contents of oxygen and other elements (including S, N, Cl, etc.) in the organic matter, i.e. $O^* = 100$

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Table 1: *Parameters used to calculate ethanol yield (see Eq:1 and Eq:2)*

Term	Definition	Tech 1	Tech 2
E_{cl}	Litres ethanol per tonne of cellulose	324	594
E_{hc}	Litres ethanol per tonne of hemicellulose	369	412
Cl_{con}	Cellulose consumed by cellulase (%)	0	0
H_{cl}	Hydrolysis efficiency for cellulose to glucose (%)	50	87
F_{gl}	The fermentation efficiency of glucose	90	95
F_{hc}	The fermentation efficiency of hemicellulose sugars	59	59
a	Mass yield of glucose per tonne of cellulose	555	966
b	Theoretical maximum yield of ethanol via fermentation (%)	51.11	51.11
c	Density of ethanol (kg dm^3)	0.789	0.789
d	Mass yield of pentoses per tonne of hemicellulose	966	1079

The Lower Heating Value (LHV), or effective heating value, is more relevant than the HHV in practical operations

$$LHV = HHV - 0.22 * H \qquad (4)$$

Where H = Hydrogen content of dry biomass (%)

There are two gasification technologies syngas and the Fischer-Tropsch (FT) method which produces a mixed range of linear hydrocarbons. Syngas technologies are still in early development. The syngas conversion efficiency of 48.8% to ethanol and 9.6% to higher alcohols. The calculations in this report only consider the ethanol potential and overall conversion efficiency of the FT technology. Hydrocracking of the waxy FT product yields 60% (by mass) diesel, 25% kerosene and 15% naphtha.
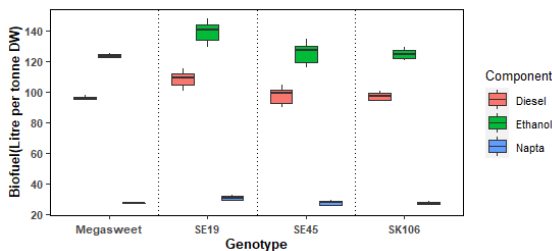
Figure 4: *Potential ethanol, diesel and Napta yield from sorghum after Fischer-Tropsch thermal conversion.*

Anaerobic digestion

Anaerobic digestion (AD) can be a sustainable means of generating energy while also valorising organic wastes.

The process involves biogas production via the microbial degradation of organic compounds in the absence of oxygen. AD reduces the bulk of organic matter to be disposed, generates digestate rich in nutrients that can be of agricultural value, and produces biogas rich in methane which can be used as fuel directly or can be converted to compressed natural gas (CNG) and liquefied natural gas (LNG).
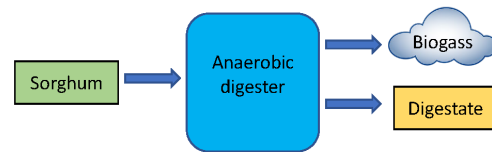
Figure 5: *Schematic representation of the conversion of sorghum biomass to biogas in an anaerobic digester.*

This value represents the experimental theoretical maximum amount of methane that can be produced from a feedstock. In addition, the properties of the digestate were also determined (Fig. 5).

Here we report the biogas production and biomethane potential (BMP) of the Sweet Sorghum varieties from this project. The biomethane potential (BMP) test was performed using active inoculum from an anaerobic digester. The inoculum has been tested for its quality and degassed to avoid interference of organic matter present in the inoculum with the test sample. The volume to head-space ratio of the digester is 7:3 and the inoculum to substrate ratio is 4:1. German standard methods (VDI 4630) were used in determining the BMP of the sample.

The dried stem and leaf samples had an average moisture content of 10.12% with a total solid content of 89.88%. The percentage of ash in the sample on wet basis and dry basis was 5.51% and 6.13%. The volatile solids percentage was 89.46% and 98.22% on wet and dry basis, respectively.

Elemental analyses were performed to determine the carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) content. The C/N ratio and C/S ratio are amongst the key indicators to identify the suitability of feedstock for mono-digestion or identifying the suitable co-digestion feedstock.

There are major differences between the leaf (Fig. 6) and stem (Fig. 7) samples. The ratio of C/N for the leaf material was 23:1 indicating that the feedstock is highly

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suitable for mono-digestion, if other necessary trace elements are added. The stem samples had a C/N ratio of 63:1 indicating that the feedstock is not suitable for mono-digestion and should be supplemented with nitrogen rich streams as co-feed.
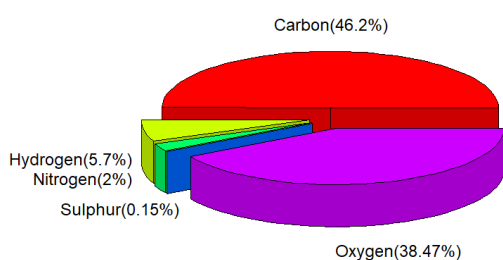

Figure 6: *Ultimate analysis of the dried sorghum leaf feedstock.*
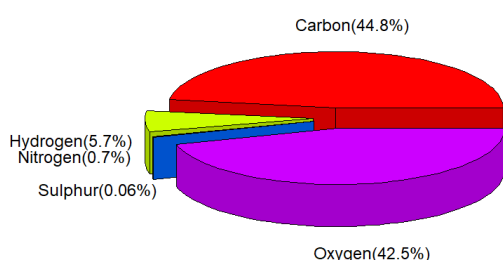

Figure 7: *Ultimate analysis of the dried sorghum stem feedstock.*

The C/S ratio of the leaf samples was 307:1 and 666:1 for the stem samples. The low sulphur content in the sample indicate that the possibility of accumulation of hydrogen sulphide in the digester is very low.

The average biogas production from the sorghum samples was 551.1 L Kg^{-1}. On Volatile solids (VS) basis, the biogas potential is 587.1 L Kg^{-1}. The weighted average methane percentage is 80.8% which is very good. The biomethane potential is 445.2 L Kg^{-1} and 474.3L Kg^{-1} on DM and VS basis respectively (Table 2).

Table 2: *Biogas and biomethane production from sorghum leaves and stems. FW refers to the material that was dried to a mositure content of 10-12% before analysis.*

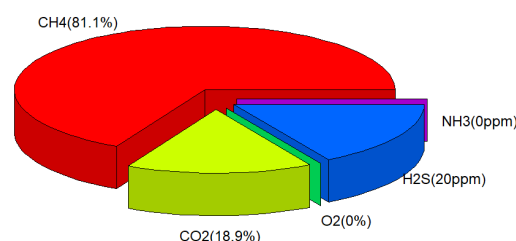| Unit	Biogas	Biomethane
	Leaves	
Litre.$Kg^{-1}VS$	488.52 ± 328.85	325.17 ± 273.59
Litre.$Kg^{-1}DW$	451.95 ± 304.24	300.83 ± 253.11
Litre.$Kg^{-1}FW$	334.38 ± 278.41	275.29 ± 231.62
	Stems	
Litre.$Kg^{-1}VS$	529.33 ± 82.34	474.31 ± 65.91
Litre.$Kg^{-1}DW$	496.88 ± 77.29	445.23 ± 61.87
Litre.$Kg^{-1}FW$	495.36 ± 69.47	400.18 ± 55.61

Figure 8: *Average gas composition after anaerobic digestion of sorghum leaves and stems.*

The biomethane levels are similar to that previously reported [2]. The bulk of the biogas (>80%) that is produced from the sorghum material is methane (CH_4). No ammonia or H_2S were present in the final gas mixture(Fig. 8).

Digestate chemical properties

The chemical oxygen demand (COD) and biological oxygen demand (BOD) of the digestate is lower than the feedstock and very low BOD indicate that the digestate resulting after the digestion is stable with very little residual biodegradable fraction.

The C/N ratio for the digestate obtained from both the sorghum leaves and stems was 8:1 indicating that majority of the C is utilised to produce biogas while the N has accumulated and is not released as ammonia. This indicates that the digestate is suitable as fertiliser in terms of C/N ratio.

However, overall the composition of the digestate is not suitable for a standalone fertiliser. The K concentrations (44517 ppm on dry mass basis) are considerably higher than N (31900 ppm on a dry mass basis). In addition, the K level is in very high compared to P (90450

ppm on a dry mass basis). The digestate from the stem samples had an even higher K content (91592 ppm on dry mass basis) than the leaf samples, while the N content was not significantly different.

However, K and P can be extracted from the digestate to be used as potash and phosphorous fertilisers, or alternatively the digestate can be re balanced to make it more suitable as a general fertiliser.

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